Soap-Based Detergent Formulations: IX. α-Sulfo Fatty Alkanolamides as Lime Soap Dispersing Agents[1]

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ABSTRACT

α-Sulfo fatty alkanolamides were prepared by sodium methylate catalyzed reactions of methyl α-sulfo fatty esters with alkanolamines, such as ethanolamine, N-methyl-2-hydroxyethylamine, diethanolamine, 3-hydroxypropylamine, 2-hydroxypropylamine, and diglycolamine. Pure compounds, such as α-sulfo palmitamides and stearamides, as well as the α-sulfo tallow amides, were prepared and evaluated as surface-active agents. The α-sulfo fatty alkanolamides were found to have excellent stability to alkali. Their stability to acid ranged from excellent in the case of α-sulfo diglycolamides to poor in the case of α-sulfo diethanolamides. Poor stability to acid was related to ease of conversion to ester-amines. Washing tests on standard soil cloths showed that the compounds were good detergents by themselves and were also effective in combination with soap and silicates. Their lime soap dispersant requirements ranged from 7-10.

INTRODUCTION

Amides of α-sulfonated palmitic and stearic acids were described by Weil, et al. (1). They were prepared by the Schotten-Baumann reaction from the corresponding α-sulfo fatty acid chlorides. The method was not entirely satisfactory because of poor yields and purification difficulties. These difficulties also limited the number and variety of amides that could be synthesized.

Our method of synthesis of alkanolamides of α-sulfo fatty acids was essentially that of Meade (2), whereby amides were prepared by reaction of amines with methyl esters of fatty acids in the presence of catalytic amounts of sodium methylate or sodium metal according to the following scheme:

$$\mathrm{RCH(SO_3Na)COOCH_3 + NH(CH_2CH_2OH)_2 \xrightarrow{NaOCH_3}}$$
$$\mathrm{RCH(SO_3Na)CON(CH_2CH_2OH)_2 \;+\; CH_3OH,}$$

where R represents a fatty acid derived long alkyl chain. The method had to be modified for synthesis of N-methyl-2-hydroxyethylamides and diglycolamides of α-sulfo fatty acids, since these both required amounts of sodium methylate substantially greater than catalytic quantities.

The objective of this investigation was to prepare lime soap dispersing agents (LSDA) which would be more stable to alkaline hydrolysis than the analogous methyl esters whose incorporation into soap-based detergents has been reported previously (3). Under acidic conditions, the α-sulfo fatty amides of secondary alkanolamines tend to rearrange to ester amines according to the following scheme:

$$\mathrm{CH_3(CH_2)_{15}CH(SO_3Na)CON(CH_2CH_2OH)_2 \xrightarrow{H^+}}$$
$$\mathrm{CH_3(CH_2)_{15}CH(\overset{\ominus}{SO_3})COOCH_2CH_2\overset{\oplus}{N}H_2CH_2CH_2OH.}$$

The analogous rearrangement of the alkanolamides of unsulfonated fatty acids was reported by Trowbridge and coworkers (4).

EXPERIMENTAL PROCEDURES

Materials

Sodium methyl α-sulfostearate and sodium methyl α-sulfopalmitate were prepared, as described elsewhere (5), and were of 95% or better purity.

Sodium methyl α-sulfotallowate (hydrogenated) was obtained as an aqueous paste designated as Bioterge TMS from Stepan Chemical Co., Northfield, Ill. The paste was dried to a powder and purified by removal of inorganic salts (absolute alcohol insolubles) and unsulfonated methyl esters (acetone solubles). Redistilled reagent grade alkanolamines were used. The ion exchange resin used was Dowex 50W X8 (Dow Chemical Co., Midland, Mich.).

Preparation and Isolation of α-Sulfo Alkanolamides

The α-sulfo alkanolamides were prepared by one of four procedures outlined below. The choice of procedure for all 18 compounds of this study is shown in Table I.

A–Preparation of N-(2-hydroxypropyl)α-sulfopalmitamide: Sodium methyl α-sulfopalmitate 33.7 g (.09 moles) was weighed into a 3 neck, 2 liter reaction flask fitted with a mechanical stirrer, Dean-Stark tube, and heating mantle. Benzene, 800 ml, was added and the solution refluxed until free of water. The solution was cooled to ca. 50 C, and 2-hydroxypropylamine 6.9 g (0.092 moles) was added followed by 0.3 g sodium methylate. The reaction mixture was refluxed for 30 min, after which time the IR analysis showed absence of the ester carbonyl band. Absolute ethanol, 800 ml, was added, the solution filtered hot, evaporated to dryness, and finally dried to constant wt in a vacuum oven at 60 C. The crude product was dissolved in 500 ml absolute alcohol, filtered to remove insolubles, and crystallized from 700 ml of 70% alcohol at -25 C. A first crop of 28.9 g was obtained, the elemental analysis of which agreed closely with the theoretical values (found: carbon, 54.63; hydrogen, 9.13; sulfur, 7.94; nitrogen, 3.20; theory: carbon 54.91; hydrogen, 9.21; sulfur 7.72; nitrogen, 3.37. The mother liquor was evaporated to dryness, and the dry residue was dissolved in 50 ml absolute alcohol and filtered. To the filtrate was added 10 ml water, and the solution was allowed to crystallize at -26 C. A second crop of 7.6 g was obtained whose IR spectrum and ash content agreed with those of the main crop. The overall yield was 36.5 g, 97%.

B–Preparation of α-sulfo tallow amides from 2-hydroxyethylamine, diethanolamine, 2-hydroxypropylamine, and 3-hydroxypropylamine: In this procedure, the reaction was carried out as described under A; however, the isolation procedure was modified. Excess alkali was removed by careful addition of Dowex 50W X8 in the acid form. The resin then was filtered off, and the amide was obtained in crude form after evaporation to dryness of the filtrate.

C–N-methyl-N-(2-hydroxyethyl)α-sulfo fatty amides: In this procedure the α-sulfo ester was dried in refluxing benzene and sodium methylate (0.4 moles/mole ester) was added, followed by the dropwise addition of N-methyl-N-(2-hydroxyethyl) amine to the refluxing solution. When the addition was complete, the solution was refluxed for 30 min, after which time, IR analysis of the product showed absence of the ester carbonyl band. The product was evaporated to dryness and excess alkali removed by careful addition of Dowex 50W X8 to an aqueous alcohol solution of

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TABLE I

Method of Synthesis and Physical Properties of Substituted α-Sulfo Fatty Amides $RCH(SO_3Na)CONR'R''$

R	R′	R″	Method of synthesis[a]	LSDR[b]	Krafft point C	Critical micelle concentration (%)
$C_{14}H_{29}$	H	CH_2CH_2OH	A	9	34.8	0.037
$C_{14}H_{29}$	H	$CH_2CH_2CH_2OH$	A	7	<0	0.035
$C_{14}H_{29}$	H	$CH_2CHOHCH_3$	A	9	<0	0.038
$C_{14}H_{29}$	CH_2CH_2OH	CH_2CH_2OH	A	7	<0	0.052
$C_{14}H_{29}$	H	$CH_2CH_2OCH_2CH_2OH$	D	7	<0	0.045
$C_{14}H_{29}$	CH_3	CH_2CH_2OH	C	9	<0	0.047
$C_{16}H_{31}$	H	CH_2CH_2OH	A	9	70.5	c
$C_{16}H_{31}$	H	$CH_2CH_2CH_2OH$	A	9	48.0	0.012
$C_{16}H_{31}$	H	$CH_2CHOHCH_3$	A	9	<0	0.011
$C_{16}H_{31}$	CH_2CH_2OH	CH_2CH_2OH	A	8	<0	0.017
$C_{16}H_{31}$	H	$CH_2CH_2OCH_2CH_2OH$	D	8	<0	0.018
$C_{16}H_{31}$	CH_3	CH_2CH_2OH	C	10	<0	0.013
Tallow derived	H	CH_2CH_2OH	B	9	70.0	---
Tallow derived	H	$CH_2CH_2CH_2OH$	B	8	48.0	---
Tallow derived	H	$CH_2CHOHCH_3$	B	9	<0	---
Tallow derived	CH_2CH_2OH	CH_2CH_2OH	B	8	<0	---
Tallow derived	H	$CH_2CH_2OCH_2CH_2OH$	D	8	<0	---
Tallow derived	CH_3	CH_2CH_2OH	C	10	<0	---

[a] See text for description of method.

[b] LSDR = lime soap dispersant requirement.

[c] High Krafft point prevents determination.

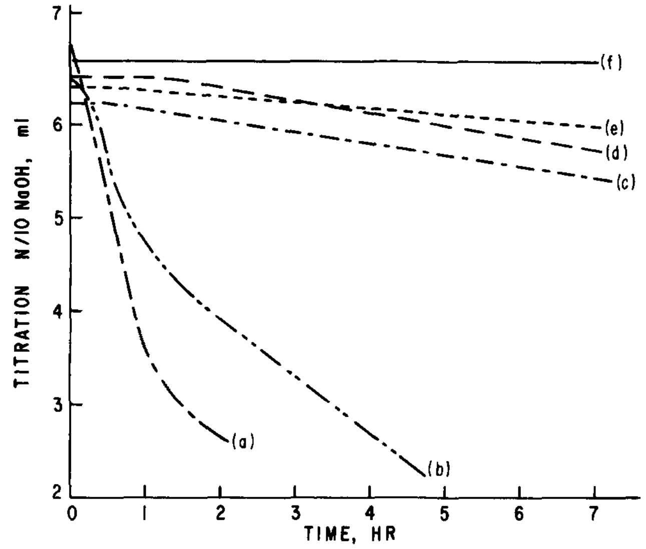

FIG. 1. Titration curves for acid stability tests of substituted α-sulfopalmitamides a, diethanolamide; b, N-methylethanolamide; c, monoethanolamide; d, isopropanolamide; e, N-(3-hydroxypropyl)-amide; and f, diglycolamide.

the product. The ion exchange resin was filtered off before crystallization.

D–Preparation of diglycolamides of α-sulfo fatty acids: This procedure was the same as procedure C, except that 1.05 moles sodium methylate/mole ester was used.

Acid Stability Studies

The various amides of α-sulfopalmitic acid were submitted to an acid stability study. A 0.01 mole sample of the test surfactant in 50 ml distilled water was refluxed with 100 ml 0.1 N hydrochloric acid. Aliquot samples were withdrawn at various intervals and titrated with 0.1 N sodium hydroxide solution to a phenolphthalein endpoint. The neutralized samples were dried and examined by IR analysis. The amount of ester formed was estimated from the ratio of the intensity of the ester carbonyl band to that of the amide carbonyl band. The titration data are represented graphically in Figure 1, and the ester content estimated from the IR data is given in Table II.

TABLE II

Rearrangement of Various α-Sulfopalmitamides to Ester by IR Spectroscopy

Amide Amide	Reaction time (hr)	Percent ester
Diethanolamide	2	65
N-Methyl-2-hydroxyethylamide	5	75
2-Hydroxyethylamide	7	7
2-Hydroxypropylamide	7	6
3-Hydroxypropylamide	7	3
Diglycolamide	7	0

Alkaline Stability Studies

An analogous series of experiments was carried out in which 0.01 mole samples of the various amides of α-sulfopalmitic acid were refluxed with 0.01 moles aqueous sodium hydroxide. There was no change in titration or IR spectra during the 7 hr reflux period.

Physical and Surface-Active Properties

The Krafft point was measured by gradually heating a 1% disperison of the test compound until a clear solution was obtained. The Krafft point data are shown in Table I.

The lime soap dispersant requirement (LSDR) was measured according to the method of Borghetty and Bergman (6). The LSDR data are given in Table I. The critical micelle concentrations (cmc) were measured by pinacyanole chloride titration (7), and the results are given in Table I.

Detergency screening measurements were carried out in a Tergotometer at 120 F in water of 300 ppm hardness. Five 4 in. circles each of EMPA 101 standard soiled cotton (EMPA), Testfabrics, Inc., standard soiled cotton-polyester blend with permanent press finish (TF), and U.S. Testing Co. soiled cotton (UST) were washed together in 1 liter detergent solution for 20 min. A commercial phosphate-built detergent was used as a control in all tests. To all test detergents, there was added 1% of detergent grade carboxymethylcellulose to prevent soil redeposition. The lime soap

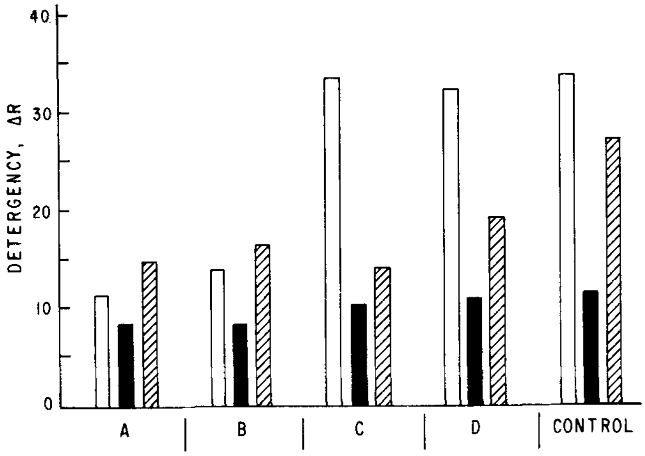

FIG. 2. Detergency bar graphs for diethanolamide of α-sulfopalmitic acid as lime soap dispersing agents (LSDA). A. LSDA at 0.04%; B. LSDA at 0.2%; C. formulation of 75% soap + 25% LSDA at 0.02%; and D. formulation of 65% soap + 20% LSDA + 1% sodium silicate (Na_2O:1.6SiO_2) at 0.2%. □ = EMPA. (EMPA 101 standard soiled cotton), ■ = UST/U.S. Testing soiled cotton), and ▨ = TF (Testfabrics, Inc., standard soiled cotton-polyester blend with permanent press finish).

dispersants were tested by themselves at concentrations of 0.04% A and 0.2% B. Unbuilt soap-based detergent formulations C, consisting of 75% tallow soap and 25% lime soap dispersant, as well as previously developed (8,9) built formulations D of 65% tallow soap, 20% lime soap dispersant, and 15% sodium silicate ($1Na_2O$:1.6SiO_2), were tested at a total detergent concentration of 0.2%. The data obtained for A, B, C, and D for the sodium salt of the diethanolamide of α-sulfopalmitic acid are shown graphically in Figure 2.

All α-sulfo fatty amides of this study were evaluated for detergency as LSDA components in formulations of type D described above. The detergency data obtained with the α-sulfopalmitamides as LSDA are shown graphically in Figure 3 and those for the α-sulfostearamides in Figure 4. Since the α-sulfo tallow amides gave detergency results similar to those shown in Figure 3, they are not included here.

RESULTS AND DISCUSSION

The syntheses of the amides of this study were straightforward, with the exception of the amides of diglycolamine and N-methylethanolamine, which required far more than catalytic amounts of sodium methylate. Whenever we attempted to prepare the amides of these two amines with catalytic amounts of sodium methylate, the desired amides were not formed. Instead, there occurred side reactions in which N-methylated amines were formed and the α-sulfo fatty esters were hydrolyzed. This reaction appears to be highly complex and has not as yet been investigated thoroughly by us.

In all amide syntheses, it was of utmost importance that all reactants were completely dry. Presence of moisture invariably brought about some hydrolysis of the starting methyl ester.

The amides are quite stable to alkaline hydrolysis in contrast to the analogous methyl esters which hydrolyze slowly in the presence of an equimolar amount of alkali (10). Thus, the α-sulfo fatty amides can be incorporated safely into alkaline detergent formulations.

Under acidic conditions, however, some of the amides underwent changes. As is shown in Figure 1, both the diethanolamide and the N-methylethanolamide of α-sulfopalmitic acid consumed acid under the test conditions. This would indicate that rearrangement, rather than hydrolysis, had occurred. This assumption was confirmed by IR data (Table II) which showed a substantial rearrangement of the two amides to the corresponding ester amines. The N-2-hydroxyethylamide, the N-2-hydroxypropylamide, and the N-3-hydroxypropylamide of α-sulfopalmitic acid showed slight consumption of acid and a correspondingly slight conversion to ester amine. The diglycolamide, on the other hand, was stable under the test conditions.

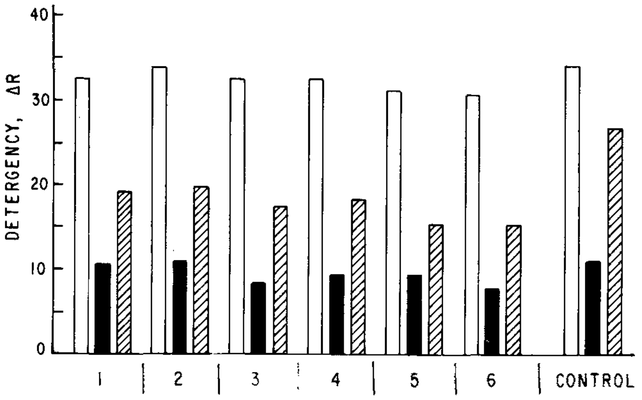

FIG. 3. Detergency bar graphs for formulations of 65% soap + 15% sodium silicate + 20% N-substituted α-sulfopalmitamide lime soap dispersing agents. Nature of amide group: 1. $-N(CH_2CH_2OH)_2$; 2. $-NHCH_2CH_2OH$; 3. $-NHCH_2CHOHCH_3$; 4. $-NHCH_2CH_2CH_2OH$; 5. $-N(CH_3)CH_2CH_2OH$; and 6. $-NHCH_2CH_2OCH_2CH_2OH$. □ = EMPA (EMPA 101 standard soiled cotton), ■ = UST (U.S. Testing soiled cotton), and ▨ = TF (Testfabrics, Inc., standard soiled cotton-polyester blend with permanent press finish).

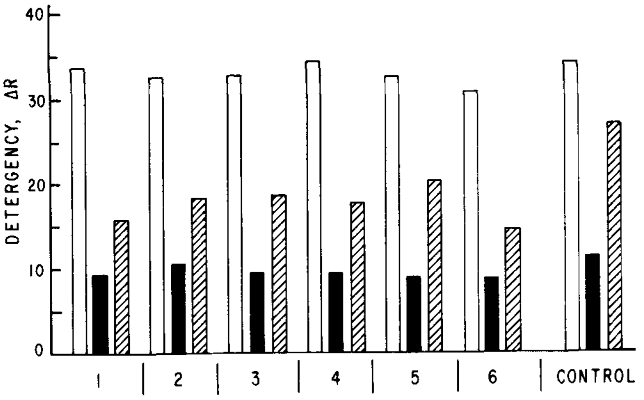

FIG. 4. Detergency bar graphs for formulations of 65% soap + 15% sodium silicate + 20% N-substituted α-sulfostearamide lime soap dispersing agents. Nature of amide group: 1. $-N(CH_2CH_2OH)_2$; 2. $-NHCH_2CH_2OH$; 3. $-NHCH_2CHOHCH_3$; 4. $-NHCH_2CH_2CH_2OH$; 5. $-N(CH_3)CH_2CH_2OH$; and 6. $-NHCH_2CH_2OCH_2OH$. □ = EMPA (EMPA 101 standard soiled cotton), ■ = UST (U.S. Testing soiled cotton), and ▨ = TF (Testfabrics, Inc., standard soiled cotton-polyester blend with permanent press finish.

The physical and surface-active properties of the amides, as shown in Table I, indicate that the solubility of the amides in water is quite high. Only the monoethanoamides of α-sulfostearic acid and of α-sulfo tallow fatty acid (hydrogenated) show high Krafft points. The LSDR of all compounds of this study vary little with chemical structure and is of the same magnitude as that of sodium methyl α-sulfotallowate, which has a value of 8 (3). The cmc values decrease, as expected, with increasing alkyl chain length of the fatty acid. Substitution of a hydroxyethyl group on the nitrogen atom of the amide or on the hydroxy oxygen atom of an N-(2-hydroxyethyl)-substituent results in an increased cmc. A comparison of the cmc values of the alkanolamides with those of the corresponding methyl esters (11) shows that the alkanolamides of the α-sulfo fatty acids possess substantially higher cmc.

The detergency behavior of the amides of this study is similar to that of the α-sulfo fatty esters (3). Figure 2 illustrates the performance of the diethanolamide of α-sulfopalmitic acid in water of 300 ppm hardness. All detergency data are expressed in terms of differences in reflectance (ΔR) after washing. The detergency of the amide by itself at a concentration of 0.04% is indicated by the three bars (A) and that at a concentration of 0.2% by the three bars (B). The graph shows that this amide is not a good detergent by itself and that the increased concentration produces only a slight increase of the detergency with EMPA and Testfabrics cloth and none with the U.S. Testing cloth. While the detergency of soap at a concentration of 0.2% in 300 ppm hard water is very poor, the detergency of a formulation containing 75% tallow soap + 25% amide lime soap dispersing agents (LSDA) at 0.2% concentration is good (Bars C). With EMPA and U.S. Testing cotton fabric, there is an obvious potentiation of detergency. Detergency on all three soiled cloths is enhanced further by the addition of 15% sodium silicate to the soap-LSDA mixture (Bars D) so that the detergency on the EMPA and U.S. Testing cloths are now ca. equal to that of the control.

The hard water detergency results of formulations of the type D consisting of 65% tallow soap, 20% LSDA, and 15% sodium silicate, where the LSDA are the α-sulfopalmitamides of this study, are shown in Figure 3, while Figure 4 shows the data for analogous formulations containing the α-sulfostearamide LSDA. As can be seen from these bar graphs, differences between the stearamides and palmitamides are slight, except for Testfabrics cloth, and the nature of the N-substituents has little influence upon detergency. The diglycolamides of both α-sulfoacids give the poorest detergencies. The N-methylethanolamide of α-sulfostearic acid gives much better Testfabric detergency than the analogous palmitamide, and the diethanolamide of α-sulfopalmitic acid performs much better than its stearamide homologue. The reasons for such anomalies are unknown. Similar detergency measurements also were made with the corresponding α-sulfo tallow amides as LSDA. The detergency data obtained with these LSDA show the same pattern as those for the palmitamides, and they were, therefore, omitted.

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